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Vibrational Dynamics of Aniline $(Ar)_1$ and Aniline $(CH_4)_1$ Clusters

by

M. R. Nimlos, M. A. Young, E. R. Bernstein and D. F. Kelley

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Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

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VIBRATION DYNAMICS IN SOLUTE/SOLVENT CLUSTERS:
ANILINE (AR)$_1$ AND ANILINE (CH$_4$)$_2$

E. R. Bernstein

Department of Chemistry
Colorado State University
Fort Collins, CO   80523

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ABSTRACT

The first excited electronic state (S_1) vibrational dynamics of aniline(Ar)$_1$ and aniline(CH$_4$)$_1$ van der Waals (vdW) clusters have been studied using molecular jet and time resolved emission spectroscopic techniques. The rates of intramolecular vibrational energy redistribution (IVR) and vibrational predissociation (VP) as a function of excess vibrational energy are reported for both clusters. For vibrational energy in excess of the cluster binding energy, both clusters are observed to dissociate. The dispersed emission spectra of these clusters demonstrate that aniline(Ar)$_1$ dissociates to all energetically accessible bare molecule states and that aniline(CH$_4$)$_1$ dissociates selectively to only the bare molecule vibrationless state. The emission kinetics show that in the aniline(Ar)$_1$ case, the initially excited states have nanosecond lifetimes, and intermediate cluster states have very short lifetimes. In contrast, the initially excited aniline(CH$_4$)$_1$ states and other vibrationally excited cluster states are very short lived (<100 ps), and the intermediate cluster 0^0 state is observed. These results can be understood semiquantitatively in terms of an overall serial IVR/VP mechanism which consists of the following elements: 1. the rates of chromophore to vdW mode IVR are given by Fermi's golden rule, and the density of vdW vibrational states is the most important factor in determining the relative [aniline(Ar)$_1$ vs. aniline(CH$_4$)$_1$] rates of IVR; 2. IVR among the vdW modes is rapid; and 3. VP rates can be calculated by a restricted vdW mode phase space RRKM theory. Since the density of vdW states is three orders of magnitude greater for aniline(CH$_4$)$_1$ than aniline(Ar)$_1$ at 700 cm^{-1} of excess energy in S_1, the model predicts that IVR is slow and rate limiting in aniline(Ar)$_1$, whereas VP is slow and rate limiting in aniline(CH$_4$)$_1$. The agreement of these predictions with the experimental results is very good and is discussed in detail.

I.   INTRODUCTION

Photoinduced unimolecular decomposition reactions are among the simplest reactions which can be studied experimentally and theoretically.   One such reaction which has received considerable attention is the vibrational predissociation of small isolated van der Waals (vdW) clusters for which one molecule is a chromophore and the other is a small "solvent" molecule.   Two dynamical events may transpire in such a system following the initial photoexcitation to S_1 vibronic levels: vibrational energy may be redistributed to modes other than the optically accessed zero order chromophore states; and at sufficient energies the cluster may dissociate.   The fundamental theoretical understanding of these two kinetic processes should be accessible in terms of Fermi's golden rule[1] and unimolecular reaction rate[2] concepts.

A.   Theoretical Considerations: T_1, T_2, IVR

The theoretical discussion of molecular vibrational dynamics is best begun by defining the concepts of small, intermediate and large molecules.[1]   The distinction between these three "cases" of vibrational dynamical behavior is based upon the number of vibrational molecular eigenstates per unit internal energy (density of vibrational states).   The zero order states accessed by optical excitation are composed of a coherent superposition of molecular (cluster) eigenstates.   As is typically the convention, T_1 refers to a population relaxation time and a loss of energy from the system. T_2 refers to a dephasing time in which the phase information of the initially excited (zero order) wavefunction(s) is lost.   IVR is basically a redistribution of vibrational energy within a system without loss of total energy.   The concept of IVR arises because the (optically accessed) coherent superposition of molecular eigenstates evolves in time and develops into other zero order, optically active (and inactive) states.   The dephasing process takes place in such a way as

to conserve total energy. This time development or evolution constitutes the IVR "T_2 time" or IVR "dynamics".

In the above context a small molecule is one in which the density of molecular eigenstates is low; so low in fact that only one eigenstate is accessed by the exciting laser pulse. In this instance, the molecular eigenstate is stationary, energy is lost only to the radiation field, $T_1 = T_2$ and no "IVR" takes place.

The intermediate molecule case arises for a higher density of molecular eigenstates. The zero order optically accessed state may be decomposed into a coherent superposition of many molecular eigenstates. If VP does not occur, the system can lose energy only by radiative processes: $T_1 = \tau_{rad}$ and T_2^{-1} = "rate of IVR". The notion of an "intermediate case" implies several (not one, not hundreds) molecular eigenstates are coherently excited by the laser pulse. Thus, typically several quantum beat components can be observed in the (wavelength resolved) emission intensity from the intermediate case molecule, as the molecular eigenstates change phase and the zero order states recur in time. One would typically see a recurring beat pattern for the intermediate case molecule.

In the large molecule limit, many (greater than ~20) molecular (cluster) eigenstates are accessed by a laser pulse and therefore the zero order optical state contains many fourier components in its dephasing or quantum beat spectrum. The summation of these many fourier components leads to an exponential time dependence - an "IVR decay" or "dissipative IVR". IVR in this case can be treated as a relaxation process and rate constants for the "decays" can be measured by characterizing the rise and fall times of zero order molecular chromophore vibronic state emission. If VP does not take place then T_2 = (IVR rate)$^{-1}$ and $T_1 = \tau_{rad}$.

If the vibrational (vdW) modes which lead to VP are coupled to the optically accessed zeroth order state, then above the VP threshold recursion times are infinite, and quantum beats do not occur. This is the typical situation in van der Waals clusters, and we expect that above the VP threshold a cluster is within the large molecule limit.

The density of states for a cluster can be estimated by the Marcus-Rice semiclassical approximation.[2] A chromophore(Ar)$_1$ cluster at ca. 250 cm^{-1} above the S_1 origin would fall within the intermediate molecule boundaries. Due to the low VP thresholds, low vibrational frequencies of vdW modes, and coupling between the zero order chromophore modes and the vdW modes, we conclude that at most accessible excess vibrational energies ($\geq$ 400 cm^{-1}) the clusters of interest to us in this work will probably fall within the large molecule limit. IVR and VP dynamics may be therefore described in general by phenomenological rate constants.

B.   Theory of IVR and VP

Theoretical studies of vibrational redistribution and dynamics including VP have been quite numerous over the last 15 years.[1-3] While we will not review the theoretical developments in detail in this report, we will present some of the important conclusions that can be drawn from the theoretical studies referenced.

Two theoretical models can be put forward for the dynamics of IVR and VP processes, and most of the available data has been interpreted in terms of one or the other of these models. These models treat IVR and VP to be either "parallel" or "serial" processes. The Beswick-Jortner[3] model for VP considers dissociation to be a process which occurs in parallel with IVR. This treatment considers the direct coupling between the chromophore vibrational states of the bound complex and the plane wave states of the dissociated complex, and is most appropriate when the amount of energy put in vdW modes by a one quanta change in the chromophore is large compared to the binding energy. Under these high energy, weak binding conditions one chromophore quantum of energy in the vdW modes must dissociate the cluster in one-half of a vibrational period. As a result, IVR/VP occurs "directly" into the "dissociative continuum". This parallel model is appropriate to diatomic/He type systems. The binding energy in the polyatomic clusters of interest in this work is typically large compared to the separations of chromophore vibrational energy levels, however. Thus, for

polyatomic clusters, the Beswick-Jortner treatment seems inappropriate and is directly at odds with the more conventional serial model based on RRKM unimolecular reaction rate theory.[2]

In the serial model,[2b] the vibrational phase space of the cluster can be divided into two regions: that of the chromophore modes and that of the vdW modes. The rationale behind this partitioning of phase space is two fold: 1) an energy mismatch exists between the vdW modes (typically less than ~50 cm^{-1}) and the chromophore modes (typically greater than ~200 cm^{-1}); and 2) the coupling between these two sets of modes is small. Optical excitation typically puts most or all of the vibrational energy into the chromophore region. The amount of energy in the vdW modes then increases as chromophore to vdW mode IVR proceeds. With the approximation that IVR among the van der Waals modes is very rapid, the VP rate can be calculated by a restricted RRKM theory in which the rate constant depends only upon the total amount of energy in vdW modes. Therefore, in this latter model, VP can occur only after chromophore to the vdW mode IVR has occurred; the rate depends essentially upon the amount of energy in vdW modes and this energy varies with time, due to chromophore to vdW mode IVR.

The two theories therefore predict much different appearance kinetics for individual vibronic states of solute/solvent clusters generated by IVR and the bare chromophore molecule generated by VP. While the interpretation of wavelength and time resolved measurements does not depend on the theoretical model imposed or envisioned, the interpretation of the cw experiments is indeed highly model dependent. Thus, in the absence of temporal resolution, the assumption of only parallel or only serial relaxation processes is important for the data interpretation. The question of serial v s. parallel processes for vibronic dynamics can in any cases be uniquely answered by time resolved studies. Indeed, we have shown zpreviously for tetrazine(Ar)$_1$,[2b] and herein for aniline(Ar)$_1$, (N$_2$)$_1$, (CH$_4$)$_1$, that the serial IVR/VP process is the appropriate one.

C   Previous Experimental Studies of IVR and VP

Studies of IVR and VP in molecular clusters available in the literature come from the laboratories of Levy,[4,5] Ito,[6] Soep,[7] Rice,[8] Paramenter,[9] Rettschnick,[10] and Bernstein.[11] In most of these instances cw (pulse width greater than 5 ns) experiments are performed on the clusters and dynamical behavior is inferred from the dispersed emission. Some time resolved dynamical studies have recently appeared on tetrazine/argon,[8,10] p-difluorobenzene/argon, the dimethyltetrazine dimer,[5,12] and the benzene/phenol dimer[13] which will be briefly discussed below.

The studies of references 4-9 involve the measurement of intensities of various dispersed emission peaks as a function of different accessed vibronic transitions in clusters. The systems studied are tetrazine$(Ar)_1$, glyoxal$(Ar)_1$, $(Kr)_1$, $(N_2)_1$, p-difluorobenzene$(Ar)_1$, pyrimidine$(Ar)_1$, $(N_2)_1$, respectively. Other work is referenced in these papers. While we will not discuss the extensive detail in these papers, we will present a general discussion of their major findings and approach to their data.

Each of the groups analyzes the cluster "dynamical" data with a particular prejudice which is often not stated. In most cases, dynamical processes are assumed to occur in parallel. Thus, IVR and VP are competitive "channels" and the various IVR "pathways" are also competitive. This point of view with regard to VP is implicit in the theoretical work of Beswick and Jortner.[3] A cluster can thereby undergo VP or IVR into several different lower modes depending on the excitation energy. In this approach the intensity of various cluster and free molecule emissions following single vibronic level excitation of the cluster yields "branching ratios" for IVR and for VP channels. The branching ratios then lead to characterization of "propensity" rules with molecular chromophore modes assigned as having a "special" relationship to VP. With the exception of the reported studies for the benzene$(Ar)_1$ cluster[8a,b] this conceptualization has led to the reporting of individual rate constants for IVR and VP for the clusters. Rate constants of the order of 10^8-10^9 s^{-1} seem to be typical. In the study of benzene$(Ar)_1$, Rice,

et al.,[8a,b] have reported only "vibrational redistribution/ predissociation" rate constants because the distinction between these two processes based solely on the presented cw measurements is not possible. We would agree with this latter position. The reporting of branching ratios and channels for IVR and VP is an outgrowth of the highly parallel conceptualization of the vibrational dynamics and cw measurements.

Bernstein, et al.,[11] have done similar cw experiments on aniline$(He)_n$, aniline$(CH_4)_1$ and, to a lesser extent, toluene$(CH_4)_n$ and have augmented these results with 2-color time of flight mass spectroscopy.

Several picosecond cluster studies on tetrazine$(Ar)_1$ have recently appeared in the literature.[10, 8c,d] The tetrazine$(Ar)_1$ studies are concerned with decay times of various vibrational states above and below the binding energy of the complex. Both excited (S_1) and ground state picosecond results have been published. The excited state studies are an appropriate preliminary effort but firm conclusions are difficult to reach based on the presented data because spectroscopic resolution could not always separate cluster and molecular emission and some of the reported lifetimes are somewhat inconsistent. Nonetheless, these studies show that the excited state IVR/VP dynamics take place on the ≤ 2 ns timescale.

The ground state data for tetrazine/argon,[8c,d] obtained by a three photon resonant fluorescence technique, indicate that little or no IVR occurs on the 15 ns timescale for S_o. The ground state IVR relaxation times are in sharp contrast to the excited state times: this difference has been explained in terms of different chromophore-vdW mode interactions in each electronic state. These authors postulate that the extent of vibrational coupling is indicated by the spectral bandshifts which occur upon clustering.

In a later paper, these authors[8c,d] also use the bandshift idea, along with our ideas of serial relaxation dictated by energy gap laws and density of states considerations, to interpret the entire relaxation/dissociation process.

Picosecond studies of the dimethyltetrazine dimer,[12] and the benzene/phenol dimer[13] have also appeared. The dimethyltetrazine

dimer study simply reports an IVR time of ~35 ps for the $6a^1$ vibronic state. This result is in reasonable agreement with the *linewidth estimated from spectroscopic data.* The benzene/phenol study reports the rate of complex disappearance following single vibronic level excitation. This rate is found to increase with excitation energy above 1275 cm^{-1}.

II.   SUMMARY OF ANILINE(X)$_1$ (X = Ar, CH$_4$) RESULTS

We have recently performed time resolved and static emission studies on aniline(X)$_1$, X = Ar, and CH$_4$, clusters. These time correlated single photon counting dispersed emission studies are still in progress and much more work needs to be done; however, the experimental and calculational results obtained thus far have elucidated the basic IVR and VP mechanisms. A summary of these results and calculations is given here.

The spectroscopy of the aniline molecule has been extensively studied,[14,15] and the most intense vibronic features have been assigned. The assignments of some of these peaks are indicated in Figure 1. The corresponding aniline(Ar)$_1$ spectrum has its origin shifted about 40 cm^{-1} to the red of the corresponding bare molecule origin. The other (vibronic) peaks are shifted by approximately the same amount. These shifts can be understood in terms of an approximately 40 cm^{-1} increase in the aniline(Ar)$_1$ binding energy upon electronic excitation. The value of the excited state binding energy is important in the interpretation of the spectroscopic and kinetic data presented below.

The dispersed emission (DE) spectrum of the aniline(Ar)$_1$ cluster following $\overline{0}_0^0$ excitation is shown in Figure 2a. (The bar over a spectral assignment indicates a cluster, rather than a bare molecule, transition.) This spectrum is very simple, and as expected, all peaks can be assigned to the vibrationless cluster. Figure 2b shows the DE spectrum following cluster excitation at 442 cm^{-1} above the $\overline{0}_0^0$. The assignment of the pumped feature is not clear and is

unimportant in the discussion here. Emission occurs from the initially pumped cluster state, and the $\overline{0}^0$ (cluster) state. Only IVR is apparent in these results, suggesting that the cluster binding energy is greater than 442 cm^{-1}. Figure 2c shows that following $\overline{6a}_0^1$ excitation (494 cm^{-1}) emission appears from both the $\overline{6a}^1$ (cluster) and 0^0 (bare molecule) states. Thus, an upper limit of 494 cm^{-1} can be put on the excited state binding energy. Interestingly, no detectable emission is observed from the lower cluster states. This observation will be discussed below.

The spectra become more complicated as the excitation energy is increased. Figure 3 presents the emission spectra arising from $\overline{15}_0^2$, $\overline{I}_0^2$, and $\overline{1}_0^1$ cluster excitation. As the cluster excitation energy increases, more bare molecule (dissociated) vibronic states become energetically accessible and are observed. In the case of $\overline{1}_0^1$ excitation, emission is observed from the $10b^1$, $16a^1$, I^1, and 0^0 states, as well as the initially pumped state. Figure 3c shows that all energetically possible final states are populated in approximately equal amounts (within a factor of 2 or 3).

We have also performed time resolved studies (time correlated single photon counting dispersed emission spectroscopy) on all of the above emission spectral features. An example of the data typically obtained is presented in Figure 4. This figure shows that the decay of the $\overline{6a}^1$ state is matched by the rise of the 0^0 state. Similar kinetics are obtained following $\overline{15}_0^2$, $\overline{I}_0^2$, and $\overline{1}_0^1$ excitation. In all cases the rise times of the final (dissociated) bare molecule states are within the experimental uncertainty of the initially populated state decay time.

Figure 5a presents the DE spectrum following $\overline{0}_0^0$ excitation of the aniline(CH$_4$)$_1$ cluster. As expected, this spectrum is very similar to the corresponding aniline(Ar)$_1$ spectrum. Very different spectra and kinetics are observed in the aniline(CH$_4$)$_1$ cluster when vibrational excitation is present, however. Figure 5b shows the DE

spectrum following $\overline{6a_0^1}$ excitation of the aniline(CH$_4$)$_1$ cluster. Two types of spectral features are present: sharp peaks which originate from the vibrationless bare molecule (0^0), and a broad emission assigned to the vdW transitions built on the $\overline{0_0^0}$ band. This latter feature is very clearly due to residual energy transferred from the $\overline{6a^1}$ mode to the vdW modes (i.e., $\overline{6a^1} \rightarrow \rightarrow \rightarrow \overline{0^0}$ + 494 cm^{-1} vdW). $\overline{6a_0^1}$ excitation for aniline(CH$_4$)$_1$ thus leads to both bare molecule 0^0 state emission and cluster $\overline{0^0}$ emission. Absent from these DE spectra for aniline(CH$_4$)$_1$ $\overline{6a^1}$ excitation is any initially excited state (i.e., $\overline{6a_1^1}$, etc.) emission. These results are in stark contrast to those found for the aniline(Ar)$_1$ cluster.

Figure 5c presents the DE spectrum which results following $\overline{15_0^2}$ excitation of the aniline(CH$_4$)$_1$ cluster. Two types of spectral features can be seen: 0^0 and much weaker $\overline{0^0}$ bands. The relative intensity of $\overline{0_0^0}$ band is found to increase upon increasing the CH$_4$/He ratio (i.e., from 0.2% to 2.0%) in the expansion gas mixture: much of this $\overline{0^0}$ emission is a result of excitation of aniline(CH$_4$)$_n$ (n>1) clusters. From the DE spectra observed following $\overline{6a^1}$ excitation we conclude that the aniline(CH$_4$)$_1$ excited state binding energy is less than 494 cm^{-1} and that the bare molecule 10b^1 and 16a^1 states are energetically accessible upon $\overline{15_0^2}$ excitation. Conspicuously absent from the DE spectra is any emission from 10b^1 (177 cm^{-1}), 16a^1 (187 cm^{-1}), or the initially excited $\overline{(15^2)}$ state. [Again we emphasize the difference between the aniline(Ar)$_1$ and aniline(CH$_4$)$_1$ spectra.]

This latter observation, in conjunction with the very high signal to noise ratio, indicates that the initially excited state has a lifetime of less than about 100 ps. Time resolved measurements indicate that the rise time of the 0^0 state is 240 ps. The disparity in these rise and decay times suggests an important question: what intermediate

states can be responsible for this kinetic difference? The most likely candidate for an intervening state in the kinetic IVR/VP process is $\overline{0}^0$. We note that when a considerable amount of energy is in the vdW modes the DE peaks are very broad, as in the case of the $\overline{0}^0$ emission in Figure 5b. Therefore, we would expect that any $\overline{0}^0$ emission in Figure 5c would also be quite broad. This breadth, in combination with the relatively short lifetime (ca. 240 ps), would make intermediate (cluster) state emission difficult to detect. The $\overline{0}^0$ cluster state must therefore be populated by IVR from the $\overline{15}^2$ state in less than 100 ps, and must live for about 240 ps prior to VP. Figure 6 presents the kinetics of the 0_0^0 base molecule transition following $\overline{15}_0^2$ cluster excitation.

III. DISCUSSION

A. The General Model

The above aniline$(Ar)_1$ and aniline$(CH_4)_1$ results are summarized in Tables I and II, respectively: these *individual* data sets cannot be explained in terms of a parallel IVR/VP mechanism. As stated above, aniline$(Ar)_1$ *dissociates into* all energetically accessible vibrational levels of the bare molecule, whereas aniline$(CH_4)_1$ dissociates only to the vibrationless level of the bare molecule. Moreover, no plausible explanation for this *difference* in dynamical behavior can be found within the framework of a parallel IVR/VP mechanism.

These data sets can be understood in terms of a serial IVR/VP model.[2b] In this model chromophore to vdW mode IVR precedes VP. Once the amount of energy in the vdW modes exceeds the binding energy, either of two processes can occur: further chromophore to vdW mode IVR, or VP. The VP rate is determined by the amount of energy in the vdW modes; the VP rate is therefore time dependent

and varies with the extent of IVR. The observed spectra and kinetics for both aniline(Ar)$_1$ and aniline(CH$_4$)$_1$ clusters systems will be the result of a competition between these two processes. The general theme for rationalizing the aniline(Ar)$_1$ and aniline(CH$_4$)$_1$ data is as follows: for the aniline(Ar)$_1$ cluster, IVR is very slow, due in part to the low density of vdW mode receiving states, and VP is very fast, because of the small (three mode) vdW phase space. For the aniline(CH$_4$)$_1$ cluster, IVR is very fast, due in part to the high density of vdW mode receiving states, and VP is relatively slow, because of the larger (six mode) vdW phase space.

We consider now each individual component of the overall redistribution/dissociation (cluster to bare molecule) process, and propose a simple model to understand the observed results.

The chromophore to vdW mode IVR in this model is simply given by the Fermi Golden rule transition probability expression: the product of a matrix element squared times a density of final receiving states. The rate of chromophore to vdW mode IVR may then be given by a product of three terms: a coupling coefficient between chromophore and vdW mode (initial and final) states; a vibrational wave function overlap term for initial and final vdW mode states; and the density of final vdW vibrational receiving states. While the above ideas have not been previously applied to the problem of chromophore to vdW mode IVR, they are not without precedent. The first two terms lead to a general "energy gap law" for IVR in which the exchange of many quanta of energy between the chromophore and vdW modes is not favored.

The qualitative results for IVR can be readily calculated: the model generates differences in the predicted behavior of aniline(Ar)$_1$ and aniline(CH$_4$)$_1$ that are at the same time both striking and in agreement with the observed results. Aniline(CH$_4$)$_1$ has six degrees of freedom in the vdW modes: one stretch, two bends and three torsions. In contrast, aniline(Ar)$_1$ has only a stretch and two bend degrees of freedom. This difference in the number of vdW vibrational modes results in very different densities of states for these two complexes. The density of vibrational states at any given energy N(E) can be estimated. For aniline(CH$_4$)$_1$ at 700 cm^{-1} of

energy, $N(E) \simeq 3 \times 10^4$ states/cm^{-1}, whereas for aniline(Ar)$_1$ at the same energy, $N(E) \simeq 15$ states/cm^{-1}. Thu., the density of vdW vibrational states is about 10^3 greater for aniline(CH$_4$)$_1$ than for aniline(Ar)$_1$ at 700 cm^{-1} of energy.

Consider now how this density of states difference can affect the IVR rates for aniline clusters: IVR should be much faster in the aniline(CH$_4$)$_1$ system than in the aniline(Ar)$_1$ system. IVR rates are measured to be on the order at a few nanoseconds in the aniline(Ar)$_1$ system and if the coupling constants are comparable for both systems, IVR rates for aniline(CH$_4$)$_1$ will be three orders of magnitude faster than those measured for aniline(Ar)$_1$ - a few picoseconds.

The VP rate constants can also be estimated for any given amount of energy placed in the vdW modes by IVR.[2] The calculations are based upon a restricted (to the vdW mode phase space) RRKM theory.[2b] For aniline(Ar)$_1$ with 700 cm^{-1} of energy in the vdW modes and a binding energy of 450 cm^{-1}, $k = (5 \text{ ps})^{-1}$ Thus, in the case of aniline(Ar)$_1$ chromophore to vdW IVR is slow and rate limiting, and subsequent VP is very fast. Any IVR process which puts energy in excess of the binding energy into the vdW modes is immediately followed by VP. All of the lower chromophore levels are populated by IVR, and as a result the bare molecule is formed in all of the energetically accessible states. This model predicts that IVR will be the overall rate controlling process for aniline(Ar)$_1$ dissociation.

Very different VP kinetics are predicted for the aniline(CH$_4$)$_1$ case. Here we find (assuming a tight transition state) that with 700 cm^{-1} of energy in the vdW modes and a 480 cm^{-1} binding energy, $k = (200 \text{ ps})^{-1}$. Thus, in sharp contrast to the aniline(Ar)$_1$ case, aniline(CH$_4$)$_1$ IVR is very fast compared to VP. IVR is expected to populate all the lower chromophore levels just as in the aniline(Ar)$_1$ case; however, in the aniline(CH$_4$)$_1$ case subsequent IVR to the $\overline{0}{}^0$ level is complete before VP can occur. Finally VP occurs slowly from $\overline{0}{}^0$ and is the rate limiting step in the entire process. This model predicts that formation of the bare vibrationless molecule will be

limited by the rate of VP for aniline$(CH_4)_1$, and will be on the hundreds of picoseconds time scale.

Thus, the observed spectra and kinetics for cluster systems in general will be the result of a competition between the two rates k_{IVR} and k_{VP}. All of the above qualitative predictions of this model are borne out by the experimental result.

B.   Numerical Simulations

We have performed detailed quantitative numerical simulations based on the above qualitative ideas.[14] These simulations which closely follow those published by us for the tetrazine/argon system,[2b] generate quantitative predictions of the spectral quantum yields and the kinetic behavior of all observed features. The calculated and observed intensities agree quite well - within a factor of two. The calculated and observed kinetics are also in good agreement - again within a factor of two in nearly all instances.

In these calculations, the probability of an IVR transition from chromophore state j to state i, P_{ij}, is given by $P_{ij} = (C_{ij}) \times$ (energy gap term) $\times (\rho_i)$, in which ρ_i is the density of vdW states at the energy $(E_{exc} - E_i)$. The quantity $(E_{exc} - E_i)$ is the total vibrational energy minus the vibrational energy remaining in the chromophore modes, and hence is the amount of vibrational energy in the vdW modes following the IVR transition. The coupling coefficients C_{ij} for any set of initial and final chromophore states and the exact functional form of the energy gap law are difficult to determine. Both depend upon the details of the potential surface. Nonetheless, some reasonable approximations can be made which result in a phenomenological theory of IVR. The notion of partioning the vibrational phase space into chromophore and vdW regions is based on the observation that the vdW mode frequencies are much lower than the chromophore mode frequencies. The comparatively slow chromophore to vdW energy transfer is due in part to this frequency mismatch. This suggests that the coupling constant C_{ij} should be inversely proportional to v_i and v_j, the chromophore vibrational frequencies.

Energy gap laws, based on wave function overlaps, have been worked out for a variety of situations.[16] The functional form of the energy gap term depends on the nature of the final states. For example, small molecules in rare gas matrices undergo vibrational relaxation to the hindered rotational degrees of freedom. In this case, the energy gap term has the functional form $\exp(-\sqrt{\Delta E})$, in which ΔE is the amount of energy transferred.[1,17] A similar form can be adopted for chromophore to vdW mode energy transfer.

The density of the vdW vibrational states is easily evaluated, if the vdW mode energies are either known or if reasonable guesses concerning their energies and anharmonicities can be made. Thus the matrix of IVR rates can be constructed with a single adjustable parameter which scales all the IVR rates.

With the above assumptions and approximations, numerical simulations of the IVR/VP process can be performed. Two population vectors, N_c and N_{nc} are defined. $N_c(i)$ is the cluster population with the chromophore in the ith vibrational level and similarly, N_{nc} refers to the bare molecule population vector. To calculate the time evolution of the population vectors three matrices must be defined: **P** is the IVR transition probability matrix with matrix elements P_{ij} for the chromophore transition to level i from level j in a time interval Δt; **K** is the VP matrix; and **R** is the radiationless transition matrix. Then

$$R_{ij} = (1-k_{isc+ic}\Delta t)\delta_{ij},$$

$$K_{ij} = (1-k_1\Delta t)\delta_{ij},$$

$$P_{ij} = \frac{A}{v_j} \exp(-\sqrt{\Delta E_{ij}}) \, \rho_i$$

in which K_{isc+ic} is the rate constant for internal conversion ($S_1 \rightarrow S_0$) and intersystem crossing ($S_1 \rightarrow T_1$) for aniline, and k_1 is the RRKM unimolecular reaction (dissociation) rate constant characteristic of an

energy (E_{exc} - E_i) in the vdW modes (see below). A is the only adjustable parameter of the model, which temporally scales the entire IVR process. The temporal evolution of the population vectors is given by

$$N_c(t+\Delta t) = \mathbf{R} \ \mathbf{K} \ \mathbf{P} \ N_c(t)$$

and

$$N_{nc}(t+\Delta t) = \mathbf{R} \ N_{nc}(t) + (1-\mathbf{K}) \ N_c(t).$$

The RRKM rate constant k_l = k(E) can easily be calculated using the Marcus Rice approximation.[2a]

$$k(E) = \frac{1}{h} \ \frac{\Sigma P(E^+)}{N(E)}$$

with $N(E) \simeq \dfrac{E^{S-1}}{(S-1)! \prod h\nu_i}$

and $\Sigma P(E^+) \simeq \dfrac{(E^+)^{S-1}}{(S-1)! \prod' h\nu_i}$,

in which $\Sigma P(E^+)$ is the sum of vibrational states above the dissociation energy excluding the reaction coordinate, E^+ = E-E_0 with E_0 the cluster binding energy, $N(E)$ is the total vibrational density of states at energy E, ν_i is the vdW mode energy and S is the number of degrees of freedom of the vdW modes. The prime on the product sign indicates exclusion of the reaction coordinate. The assumption made in these calculations is that the cluster transition state is a "tight binding" one.[17] The calculation of RRKM rates is explained in detail in ref. 2.

The IVR rates in the aniline(Ar)$_1$ case are rather sensitive to the densities of states. In this case, the values of ρ_i (=N(E)) used in the construction of the IVR transition probability matrix are calculated with a direct count method.[18] Vibrational frequencies of

45 cm^{-1} (stretch), and 15 cm^{-1} (both bends) and anharmonicities of 3% (i.e., $\Delta v_{i,\ i+1}$ /$\Delta v_{i-1,i}$ = .97) are assumed.

Quantitative predictions of the model can be made from the simulation procedure described above. The results of these simulations, in terms of kinetics and spectral quantum yields, are compared with the experimental results in Tables I and II. In all cases the agreement is quite good; within a factor of about two.

Several comments and observations about these calculations and their comparison to the experimental data can be made. The experimental results show that the extent of vdW vibrational overlap tends to decrease with increasing energy change in an IVR transition. This can be seen from the results in Table I. For example, following aniline(Ar)$_1$ $\overline{1}^1_0$ excitation, the 0^0, $10b^1$, $16a^1$ and I^1 final product states are formed in approximately the same amounts. If the vibrational overlap were energy independent, then the 0^0 state would be somewhat favored due to the higher density of vdW states corresponding to that level. Energy gap laws are simply generalizations of how vibrational overlaps vary with the energy difference between states. The functional form of the energy gap law used is chosen rather arbitrarily - basically large energy chromophore transitions are not favored.

The assumed energy gap law, in combination with the calculated density of vdW states, determines the calculated energy dependence of IVR transition rates. The calculations predict that for aniline(Ar)$_1$ IVR from the initially excited state is far slower than subsequent IVR transitions. Thus, the calculated final state rise times closely match the initially excited state decay times, in agreement with the experimental results.

VP is predicted to be the rate limiting process for aniline(CH$_4$)$_1$. The calculated VP rate for $\overline{6a}^1_0$ excitation depends strongly on the assumed binding energy, E$_0$. With an assumed E$_0$ of 480 cm^{-1} the calculated $\overline{6a}^1$ VP rate is (160 ns)$^{-1}$. The vast majority of emission would be from the cluster $\overline{0}^0$ state and not the bare molecule 0^0 state,

in agreement with the observations. The calculated VP rate for $\overline{15_0^2}$ excitation is 100 ps, again in good agreement with the experimental results.

The most severe approximation in this calculation is that the IVR transition matrix P is scaled by a single constant coupling parameter for all modes. This approximation is surely not completely correct; however, the agreement between the experimental and calculated results suggests that this approximation is good to within a factor of about two.

C   Comment on Techniques and Modeling.

A word of caution concerning the general experimental techniques for this research is in order. We have consistently found that the most difficult and time consuming portion of this research is *definitely not* the picosecond time resolved measurements as one might naively expect. Time correlated single photon counting dispersed emission measurements are "simply" calibrated by obtaining an accurate instrument response function on low level scattered light at regular intervals and by keeping the overall photon arrival rate below 1000 counts/s. The two most difficult aspects of these studies are the old spectroscopic problems of sample characterization and transition assignments. System characterization is especially important for these kinetic studies because the IVR/VP kinetics are sensitively dependent on the size of the cluster. Thus, if IVR/VP rates in aniline(CH_4)$_1$ are desired, the expansion system must be arranged to keep the concentration of aniline(CH_4)$_n$ (n>1) clusters below the limit of detection. We find typically that for an expansion pressure of 2500 torr of helium carrier gas, both the aniline and methane pressure should be ≤10 torr. If the methane mixing pressure is increased by a factor of five or so, significant distortion in both the emission spectrum and the rise and decay times of the various features is quite pronounced. Moreover, new cluster features appear in the emission spectrum of high methane concentration expansions that can be misinterpreted as arising *from*

aniline$(CH_4)_1$ clusters. If these methane concentration dependent features are incorrectly assumed to arise from the n = 1 cluster, the entire IVR/VP scheme will be misunderstood and the assigned IVR/VP lifetimes will appear to be much different than they actually are. We suspect, for example, that much of the reported tetrazine$(Ar)_1$ kinetic data, which has often been obtained for tetrazine in pure argon expansions, is so distorted.[8,10]

IV. CONCLUSIONS

The main conclusions of this work can be summarized as follows:

(1) Aniline$(Ar)_1$ and aniline$(CH_4)_1$ clusters exhibit much different S_1 vibrational dynamics. Aniline$(Ar)_1$ undergoes IVR relatively slowly (nanoseconds), and all energetically accessible bare molecule states are populated by VP. In contrast, aniline$(CH_4)_1$ undergoes rapid IVR (<100 ps) and only the 0^0 level is populated by VP from $\overline{0^0}$.

(2) The dynamical differences between aniline$(Ar)_1$ and aniline$(CH_4)_1$ can be understood in terms of a serial IVR/VP model. In this model, the rate of IVR is given by Fermi's golden rule, and the rate of VP is given by a restricted RRKM theory with regard to both IVR and VP processes.

(3) The density of vdW vibrational states is the single most important factor in determining the dynamical differences between aniline$(Ar)_1$ and aniline$(CH_4)_1$.

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TABLE II: Aniline$((H_4))_1$ relative spectral intensities, risetimes and decay times. The intensities are normalized to that of the 0⁰ transition. Calculated values are in parentheses.

Cluster Excitation	Initially Excited Decay Times (ns)	Product State Rise Times (ns)	Initially Excited State Intensity	Product State Intensity[a]	
				$\overline{0^0}$	0^0
$6a_0^1$	<0.1 (10^{-3})	(160)	0 (0)	20 (20)	1.0 (1.0)
15_0^2	<0.1 (10^{-3})	.24 (.18)	0 (0)	0 (0)	1.0 (1.0)

a) states not identified have zero calculated and observed intensity

TABLE I: Aniline(Ar)$_1$ relative spectral intensitites, rise times and decay times. The intensities are normalized to that of the 0° transition. Calculated values are in parentheses.[a]

Cluster Excitation	Initially Excited State Decay Times (ns)	Product State Rise Times[b] (ns)	Initially Excited State Intensity	Product State Intensities			
				1^1	$16a^1$	$10b^1$	0°
$6a_0^1$	4.7 (4.3)	4.7 (5.2)	1.6 (1.2)				1. (1.)
$\overline{15}_0^2$	1.5 (1.9)	1.5 (2.0)	4.7 (1.3)		1.0 (.59)	1.6 (.83)	1. (1.)
$\overline{1}_0^2$	c (1.7)	1.0 (1.8)	c (.72)	(.59)	.57 (.59)	1.0 (1.0)	1.1 (1.1)
$\overline{1}_0^1$	2.7 (2.3)	2.7 (2.5)	1.9 (1.1)	.76 (.11)	1.0 (.62)	.9 (.72)	1.0 (1.0)

(a) Franck-Condon factors of the 1_1^1, $16a_1^1$, and $10b_1^1$ sequence transitions are assumed to be unity.

(b) Rise curves generated from the simulations are slightly non-exponential, but are similar to the fitted exponential rises.

(c) Not observed.

Figure Captions.

Figure 1. Time of flight mass selected excitation spectrum of bare aniline, in a molecular jet. Several of the more intense vibronic transitions are assigned.

Figure 2. Dispersed emission spectra of aniline(Ar)$_1$ following excitation at a) $\overline{0_0^0}$, b) 442 cm^{-1} and c) $\overline{6a_0^1}$ (494 cm^{-1}). Assignments of the more intense features are indicated.
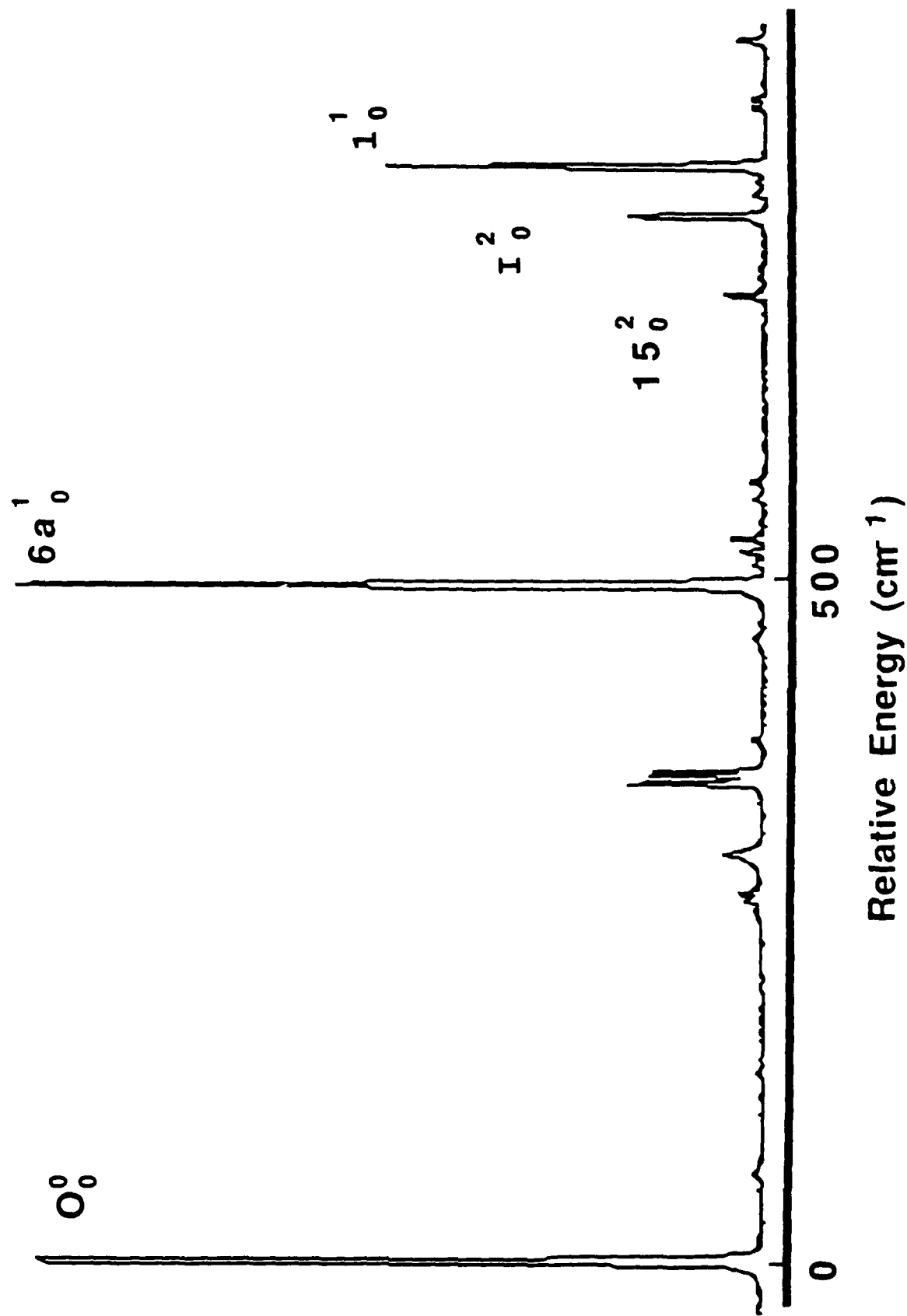
Figure 3. Dispersed emission spectra of aniline(Ar)$_1$ following excitation at a) $\overline{15_0^2}$ (718 cm^{-1}), b) $\overline{I_0^2}$ (749 cm^{-1}) and $\overline{1_0^1}$ (803 cm^{-1}). Assignments of the more intense features are indicated.

Figure 4. Emission kinetics following $\overline{6a_0^1}$ excitation of aniline(Ar)$_1$. The kinetics of the $\overline{6a_0^1 I_2^0}$ and $\overline{0_0^0}$ transitions are shown. Also shown are calculated curves corresponding to a) a 4.7 ns decay, and b) a 4.7 ns rise and a 7.6 ns decay.

Figure 5. Dispersed emission spectra of aniline(CH$_4$)$_1$ following excitation at a) $\overline{0_0^0}$, b) $\overline{6a_0^1}$ (494 cm^{-1}), and c) $\overline{15_0^2}$ (718 cm^{-1}). Assignments of the more intense features are indicated.

Figure 6. Emission kinetics following $\overline{15_0^2}$ excitation of aniline(CH$_4$)$_1$. The kinetics of the 0_0^0 transition are shown. Also shown is a calculated curve corresponding to the convolution of the instrument response function with a 240 ps rise and a 7.6 ns decay.
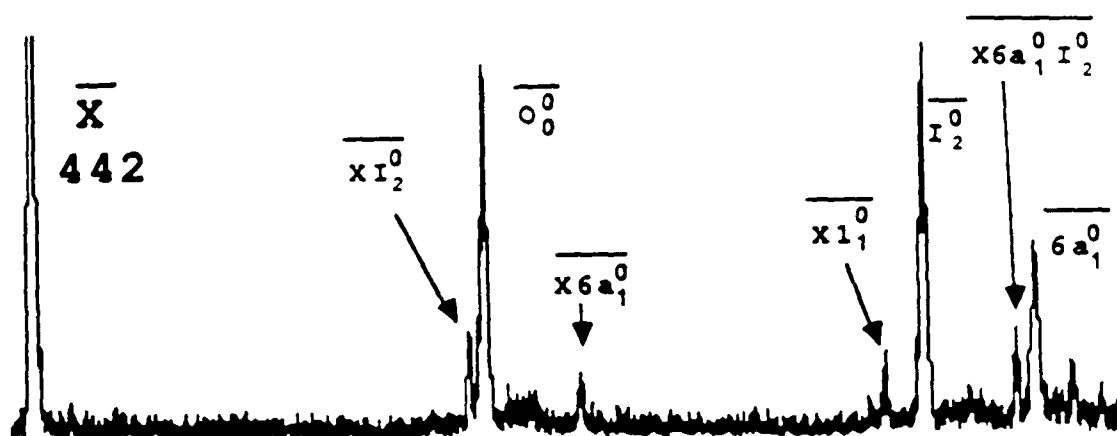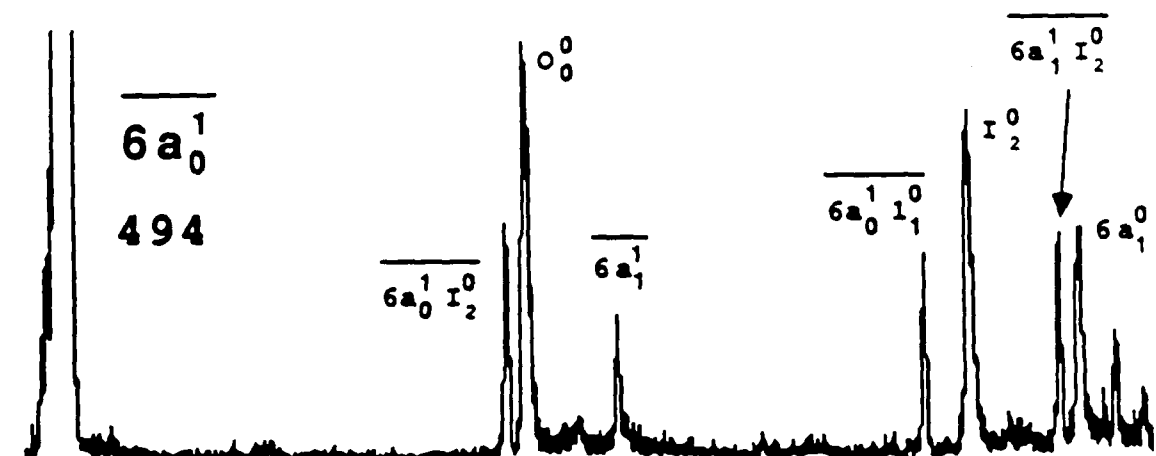
TOFMS Aniline

0_0^0

$6a_0^1$

15_0^2
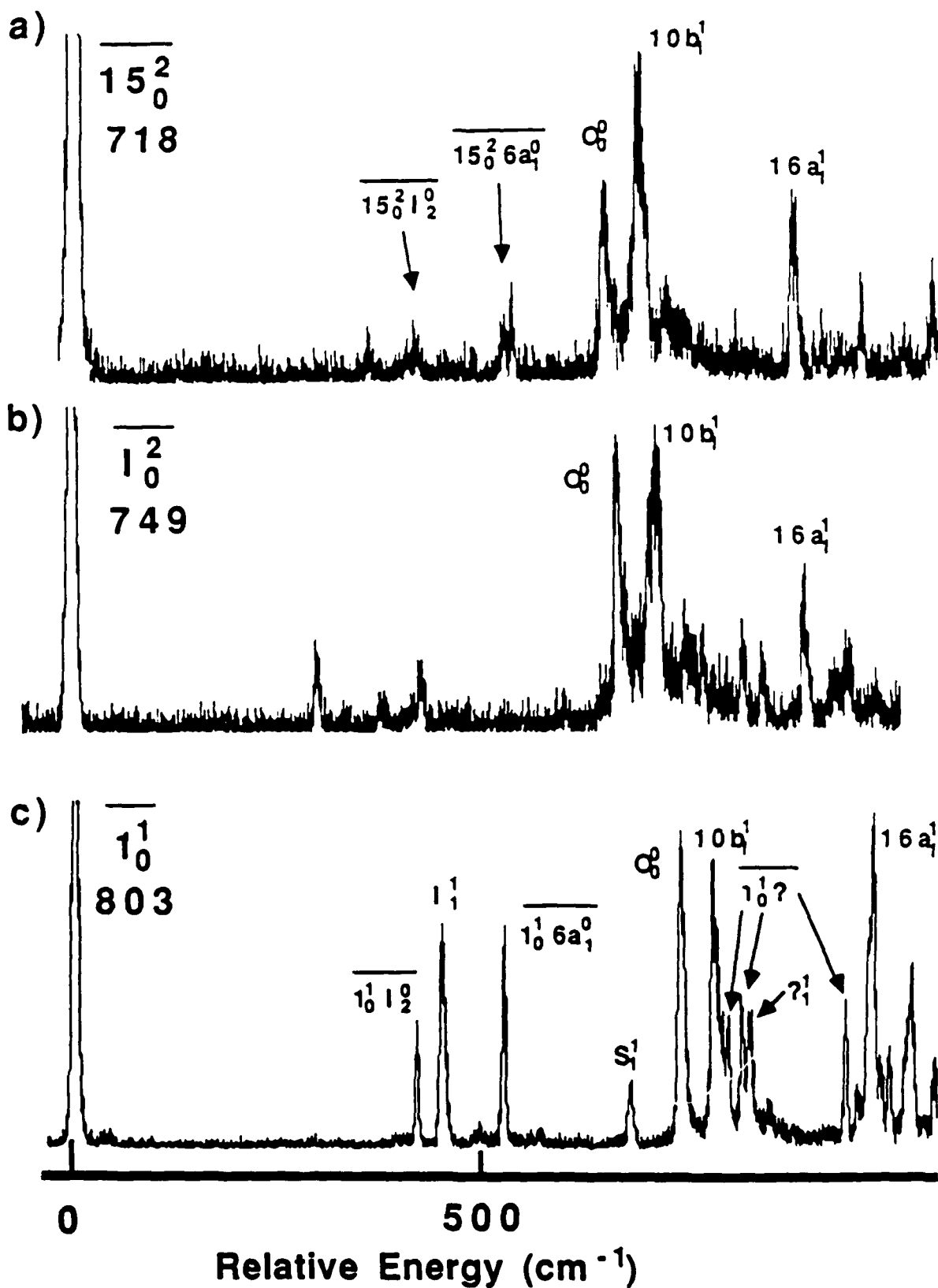
I_0^2

1_0^1

Relative Energy (cm^{-1})

0

500

Fig. 1

Aniline(Ar)$_1$ DE

a)

$\overline{O_0^0}$ $\overline{I_2^0}$ $\overline{6a_1^0}$ $\overline{1_1^0}$

b)

$\overline{X}$
442

$\overline{XI_2^0}$ $\overline{O_0^0}$ $\overline{X6a_1^0}$ $\overline{X1_1^0}$ $\overline{I_2^0}$ $\overline{X6a_1^0 I_2^0}$ $\overline{6a_1^0}$

c)

$\overline{6a_0^1}$
494

$\overline{6a_0^1 I_2^0}$ O_0^0 $\overline{6a_1^1}$ $\overline{6a_0^1 1_1^0}$ I_2^0 $\overline{6a_1^1 I_2^0}$ $6a_1^0$

Relative Energy (cm^{-1})

0   500

Aniline(Ar)$_1$ DE

a) $\overline{15^2_0}$
718

$\overline{15^2_0 1^0_2}$
$\overline{15^2_0 6a^0_1}$
O^0_0
$10b^1$
$16a^1_1$

b) $\overline{1^2_0}$
749

O^0_0
$10b^1$
$16a^1_1$

c) $\overline{1^1_0}$
803

$\overline{1^1_0 1^0_2}$
1^1_1
$\overline{1^1_0 6a^0_1}$
S^1
O^0_0
$10b^1$
$\overline{1^1_0 ?}$
$16a^1_1$
$?^1_1$

0   500

Relative Energy (cm^{-1})

a)

b)

Time (nsec)

Aniline(CH$_4$)$_1$ DE

Time (nsec)
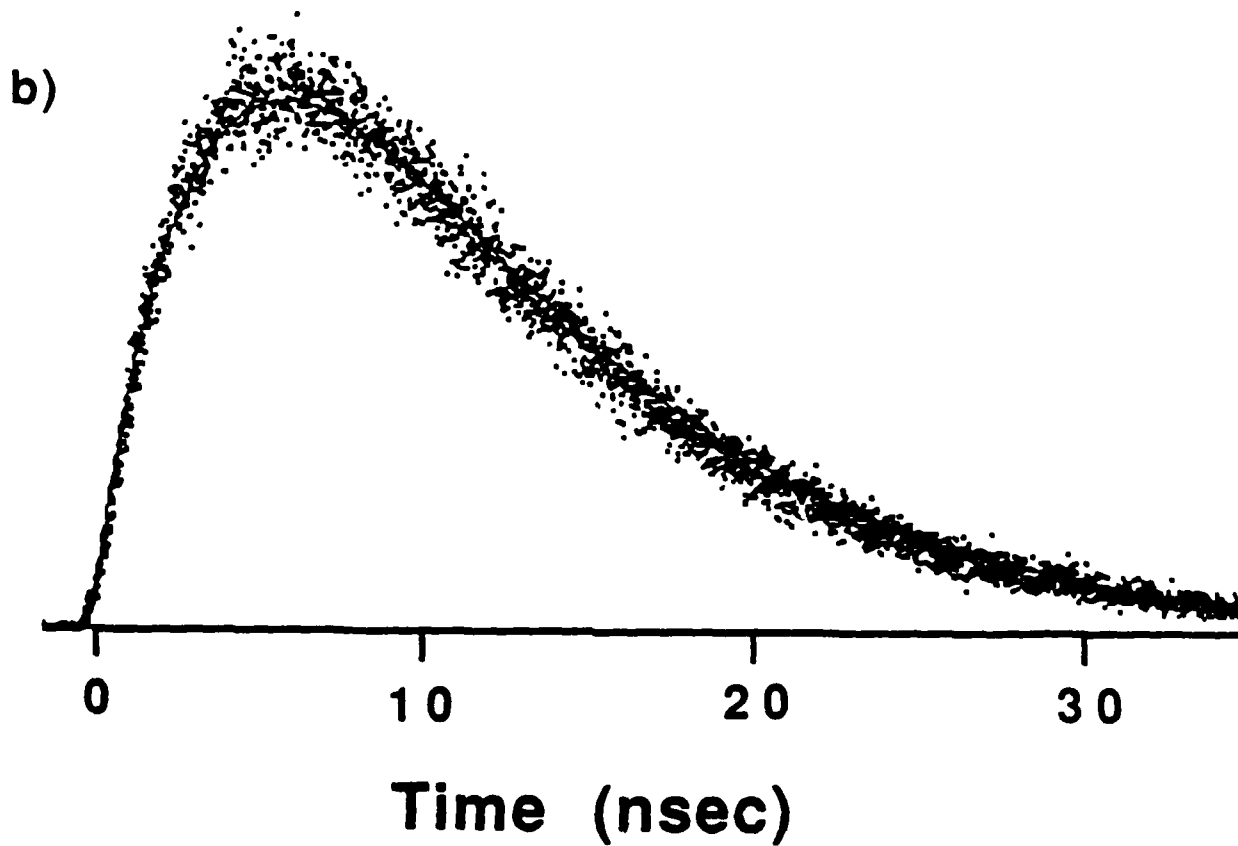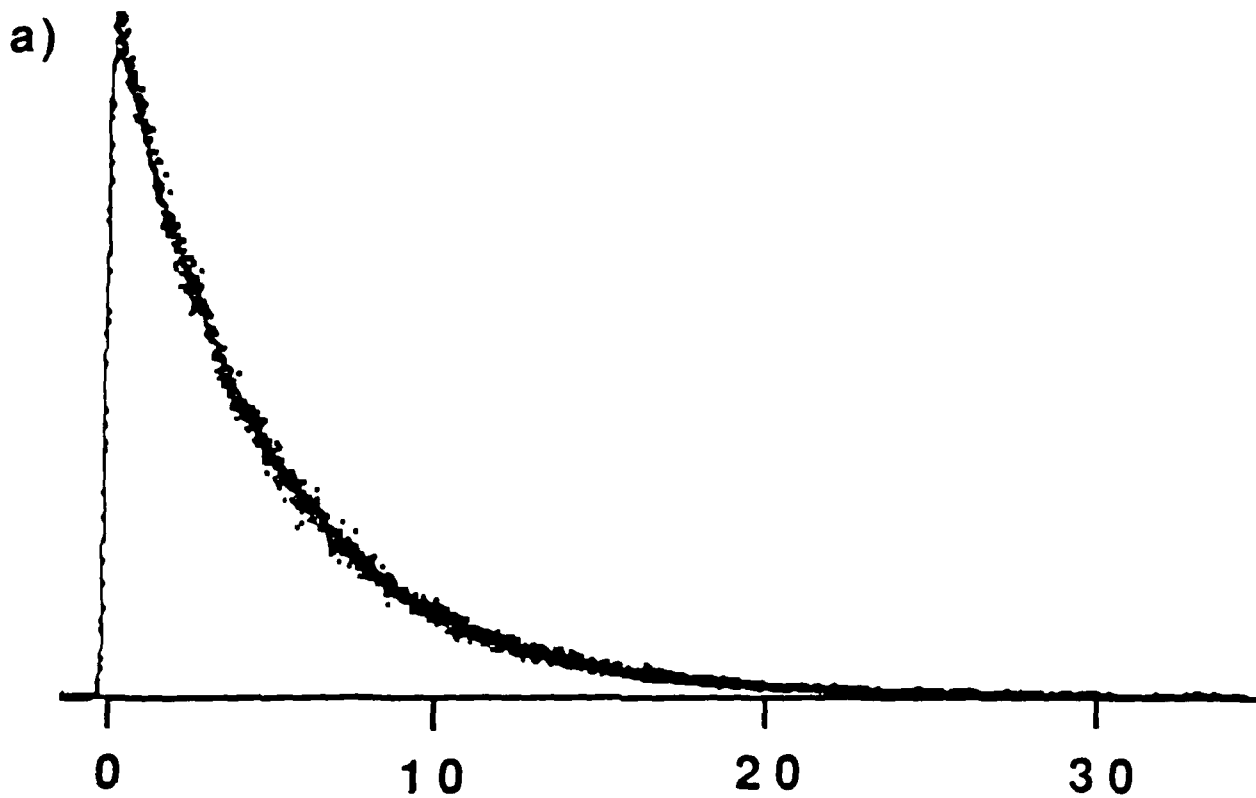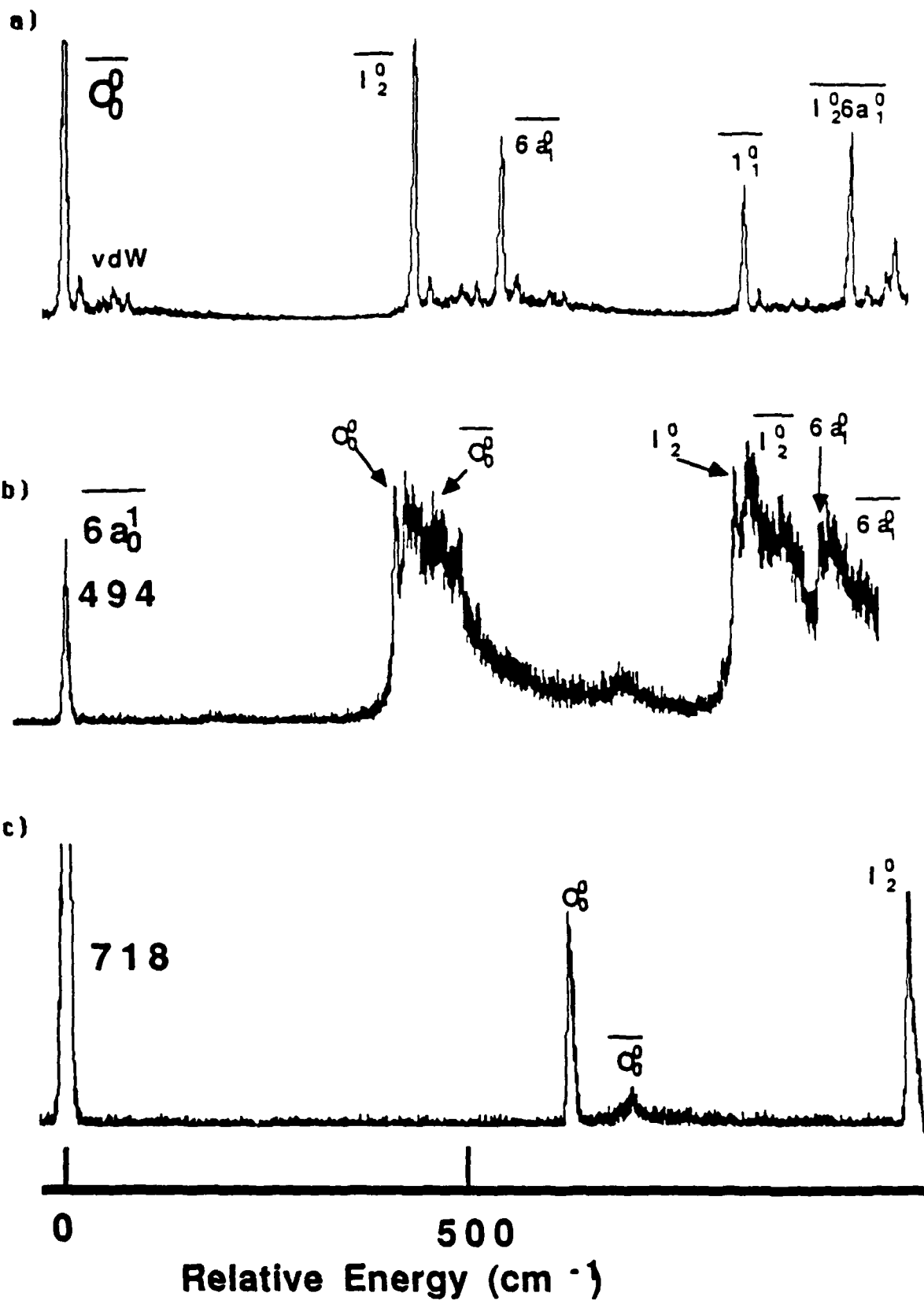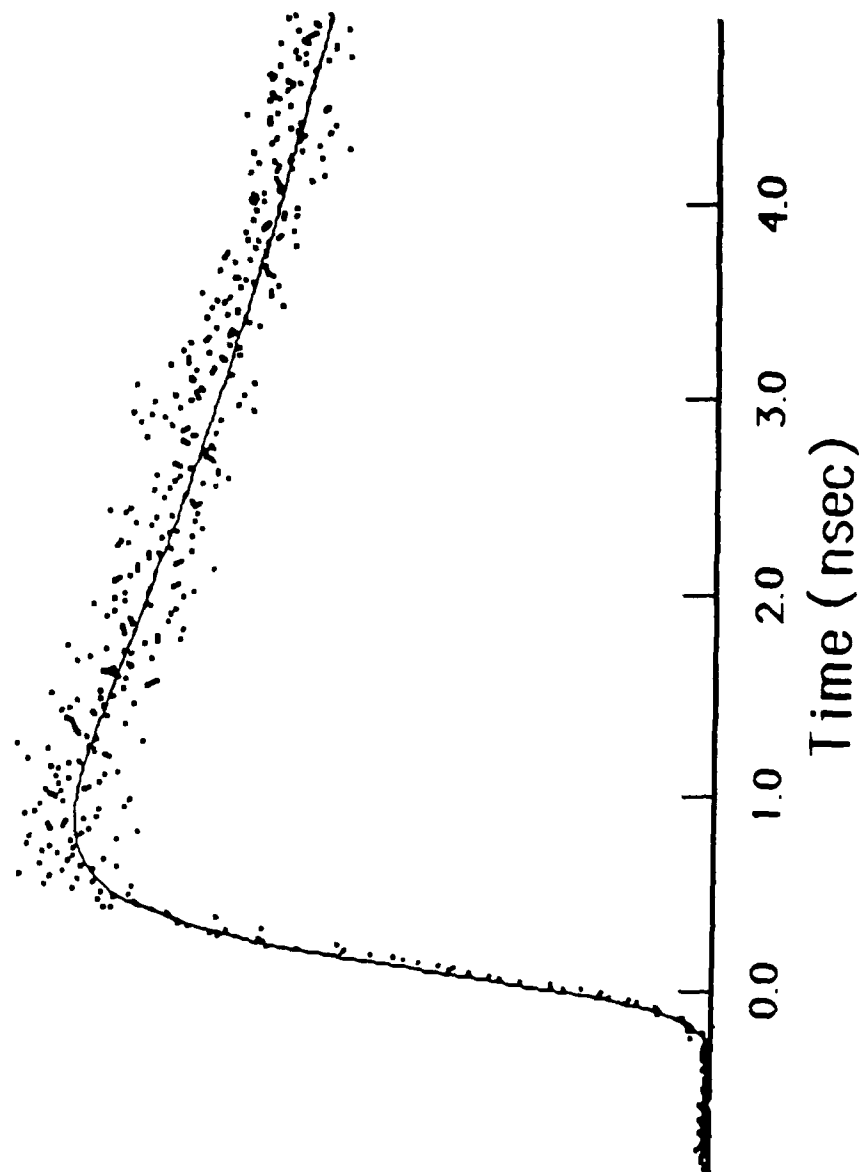
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